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EXHIBIT A

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71 Applicant(s): Public organization:
Centre National de la Recherche
Scientifique (CNRS) – France.

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72 Inventor(s): Bocquilon, Geneviève;
Bogicevic, Christine; Loriers-Susse,
Christine; and Loriers, Jean.

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74 Agent: Nony & Company Law Firm

54 Process for the preparation of single crystals of cubic boron nitride.

57 Process for the preparation of single crystals of cubic boron nitride by conversion of hexagonal boron nitride in the presence of a catalyst containing at least one alkaline or alkaline-earth nitride in an HP-HT apparatus by operating under appropriate pressure and temperature conditions, characterized in that at least one additive element chosen from aluminum, boron, silicon, zirconium and titanium is added to said catalyst.

The purpose of the present invention is a process for the preparation of single crystals of cubic boron nitride.

It is known that boron nitride has several crystalline forms: the hexagonal graphite-type form (h-BN), the hexagonal wurtzite-type form (w-BN), and the cubic blende-type form (c-BN).

Cubic boron nitride is currently the hardest material known after diamonds. Compared to diamonds, it has the advantage that it reacts little with iron-based transition metals and withstands high temperatures better. For this reason, it is used as an abrasive material in the manufacture of grinding wheels and cutting tools, as well as in the machining and polishing of hard alloys when in the form of a fine powder.

Cubic boron nitride may be prepared using a hexagonal form at high-pressure and high-temperature (HP-HT) either by shock wave action or by static compression at a pressure greater than 10 GPa and a temperature greater than 2,000°C. However, the dimensions of the crystals obtained are very small, in the order of micrometers, and the conversion yield is not very high.

Various inventors have succeeded in increasing the yield and lowering the pressure and temperature conditions in the conversion of h-BN to c-BN by adding to the starting product additives capable of forming with it a eutectic mixture that produces a liquid phase at temperatures less than 2,000°C. c-BN crystallizes using the obtained solution. Given that the pressure required to transform h-BN to c-BN varies directly with the temperature, the use of these additives has also allowed for operation at less elevated pressures. Of these additives, which are called solvents, catalysts or initiators depending on the situation, the most commonly used are alkaline or alkaline-earth nitrides. To review the different c-BN preparation methods, one may cite for example E. Rapoport, *Ann. Chim. Fr.* 10, p. 607-638 (1985).

The known c-BN manufacturing processes using catalysts provide crystals whose maximum dimensions are generally in the order of approximately 0.25 mm. In addition, the obtained crystals often have an irregular or non-compact shape that makes them more or less brittle. For certain applications such as the manufacture of tools intended for use in severe conditions, it is necessary to have a very wear-resistant abrasive whose grain dimension exceeds 0.25 mm.

One has now discovered that it is possible to obtain good quality, single c-BN crystals whose dimensions may reach 0.5 mm and a satisfactory morphology through the conversion of h-BN in HP-HT conditions in the presence of a nitride catalyst without introducing crystallization nuclei, but by adding at least one particular additive element to the catalyst. In the process according to this invention, the conversion yields as well as the temperature and pressure conditions are comparable to those of known processes. However, compared to the crystals produced using traditional solvents-catalysts mentioned above, the c-BN crystals obtained according to this invention have larger dimensions as well

as improved morphology and quality.

Therefore, the purpose of the invention is a process for the preparation of single crystals of cubic boron nitride by conversion of hexagonal boron nitride in the presence of a catalyst containing at least one alkaline or alkaline-earth nitride under appropriate HP-HT conditions, characterized in that at least one additive element chosen from aluminum, boron, silicon, zirconium and titanium is added to said catalyst.

Thanks to this invention's process and in working under optimal conditions, one can obtain single crystals having in particular dimensions greater than 0.25 mm. The crystals are of a good quality with flat surfaces and sharp edges.

In particular approaches, the invention's process may also present the following individual or combined characteristics.

One operates in a HP-HT-generating device whose principles are well known. For example, one can refer to US patent 2,947,617 or the article by E. Rapoport mentioned above, which describe, among other elements, the temperature and pressure conditions corresponding to the respective stability ranges for h-BN and c-BN.

h-BN may be introduced in powder form with, for example, particle sizes less than approximately 50 μm , and in particular approximately 40 μm . The powders of the nitride catalyst and additive elements that are preferably mixed before use have particle dimensions less than 100 μm for example, and in particular less than approximately 60 μm . This mixture comprising the catalyst may be mixed with the hexagonal boron nitride before introducing it into the HP-HT device cell, or it can also be introduced into the cell in alternating layers of h-BN and the catalyst mixture.

In bringing this mixture to a temperature at least sufficient for a liquid phase to appear, the hexagonal BN dissolves in the liquid phase (or flux) and using this solution, c-BN crystallizes if the temperature and pressure conditions correspond to c-BN's range of stability. These conditions are known, as noted earlier.

One keeps the reaction mixture at the selected temperature and pressure conditions for a sufficient duration to permit the optimal growth of crystals, then one subjects said mixture to quenching, that is a rapid cooling, which in practice amounts to interrupting the heating, and finally one returns the reaction mixture to ordinary atmospheric pressure.

The pressure and temperature conditions as well as the reaction duration and the optimal proportions of the reactants may be pre-determined in each case by simple routine experiments. The h-BN proportion in the starting mixture is obviously greater than the saturation of the flux at the temperature and pressure conditions used. In other words, one operates with an excess of h-BN.

Generally, the proportions by weight of h-BN in relation to the catalyst (including the additive) may vary in the range from 1 to 20.

The proportions by weight of the additive element in relation to the alkaline or alkaline-earth nitrides may vary for example in the range from 0.05 to 1.

One operates at a selected, pre-determined pressure for example between approximately 4.5 and 7 GPa. Generally, one operates at a temperature greater than 1,350°C, preferably at least equal to 1,500°C, and less than 2,000°C. Even though an increase in temperature generally enhances obtaining quality crystals, one should note that in certain cases increasing the temperature above a certain limit may result in reduced quality and/or dimension of the crystals. Also, one shall generally select the temperature as a function of the pressure at which one wishes to operate, and in particular as a function of the capabilities of the HP-HT device used, since as already mentioned above, these two conditions are interrelated, whereby the h-BN conversion pressure increases with the temperature in a given system.

The optimal temperature and pressure conditions may thus be determined in each case through routine experiments.

Similarly, the optimal proportion of the additive element (Al, Si, B, Zr, Ti) in relation to the alkaline or alkaline-earth nitride may easily be determined in each case by experimentation.

One notes that at constant pressure and temperature, one requires a minimum proportion of the additive to obtain crystals with satisfactory dimension and quality. By increasing the proportion of the additive, the quality of the c-BN crystals obtained diminishes.

After having brought the starting mixture to the selected temperature and pressure, one maintains the reaction mixture at these conditions (T, P) for a sufficient, pre-determined period of time to allow optimal growth of crystals. This time period that may range from 1 to 20 minutes is generally between 1 and 5 minutes long approximately.

One then stops the heating process to perform a temperature tempering, and then one returns the pressure to the ambient value.

The c-BN crystals obtained may then be separated and purified by known means, in particular by taking advantage of the differences in the chemical or physical properties between h-BN and c-BN. For example, c-BN is not corroded by the fluoridating mixture ($\text{NaF} + \text{H}_2\text{SO}_4$), in contrast to h-BN. One can also separate these two forms of boron nitride by using their differences in density, for example according to usual methods of flotation in a dense medium like bromoform.

Of the nitrides that constitute one of the ingredients of the catalytic mixture according to this invention, one shall mention in particular the alkaline and alkaline-earth nitrides and boronitrides, in particular: Li_3N , LiBN_2 , $\text{M}^{(\text{II})}_{\text{leg}}\text{N}_2$ and $\text{M}^{(\text{II})}_{\text{leg}}\text{B}_2\text{N}_4$ with $\text{M}^{(\text{II})}_{\text{leg}}$ representing Ba, Ca, Sr, or Mg.

The invention is illustrated by the following examples:

Example 1:

A "belt" type device is used having a usable volume of 0.5 cm³. Fig. 1 depicts a schematic axial cross-section of its central portion that comprises within the enclosure delineated by walls 1 and pistons 2 and 3, capsule 4 containing the reactive mixture 5. Capsule 4, comprised for example of a tube of sintered h-BN has on its interior a vessel made of graphite 6, itself surrounded by an anhydrous, insulating material (part 7, comprised for example of a halogenic NaCl_{0.5}Br_{0.5} mixture or by dehydrated pyrophyllite), then a part made of pyrophyllite 8. Parts 9, 10, and 11 are respectively comprised of pyrophyllite, steel and molybdenum. Parts 10 and 11 serve to conduct electrical current to the vessel.

The pressure is determined by known methods (see US 2,947,617 for example) by using an initially calibrated device that allows linking the applied force (deducted from the pressure in the primary hydraulic circuit) to the pressure in the cell. This calibration is performed at 20°C and uses locations of discontinuities in electrical resistance of metal reference samples, which are produced at known pressures, for example: Bi at 2.54 and 7.7 GPa; Ti at 3.7 GPa; and Ba at 5.5 GPa. The temperature is deduced from the heater power by using calibration curves of the temperature as a function of power, established at high pressure using chromel-alumel thermocouples or Pt-Pt10%Rh.

The tests were conducted using a starting mixture containing a nitride (Ca₃N₂, Mg₃N₂, Li₃N), a powder of an element M (M=Al, B, Si, Ti) and by using hexagonal boron nitride in powder form, sold by the Carborundum Co., USA, containing 0.2% oxygen and whose particle dimensions are less than 40 µm. In the cell, one arranges alternating layers of the starting mixture with the hexagonal boron nitride. For example, in all tests mentioned later on, the ratio of the weight of h-BN to the starting mass is equal to 8, a value considerably greater than that corresponding to the flux saturation. The treatment durations at (P, T)_{max} (maximum pressure and temperature for the treatment) are 3 minutes long, followed by quenching at P_{max}, obtained by interrupting the heating, then followed by a decompression.

The c-BN formed by the reaction products is separated by chemical treatments that allow the successive solubilization of:

- the catalytic solvent by an acid attack (HCl) or by water depending on the catalyst;
- the hexagonal boron nitride that has not reacted and silicates that may have originated from the cell, by a fluoride mixture (NaF + H₂SO₄);
- the graphite originating from the vessel, by a sulpho-chromic attack (CrO₃+H₂SO₄).

If h-BN and the graphite are present in large quantities, these treatments are followed by separation using a dense liquid like bromoform.

The cubic boron nitride was identified by X-ray diffraction. The crystals were examined through a binocular magnifier and their morphology was characterized using an electronic scanning microscope.

Example 2:

Table 1 provides examples of starting mixtures that were used to manufacture c-BN in the process described above as well as indications pertaining to the influence of the proportions of M in this mixture on the minimum pressure to synthesize compact, c-BN crystals at 1,700°C. In this table, the percentages of the additives are by mass and relate to the mass of alkaline or alkaline-earth nitride. The percentages marked with an asterisk are considered minimum percentages. As a reminder, the ratio of the mass of h-BN to the catalytic mixture here is 8.

Table 1

Nitride	M	$\frac{M}{\text{nitride}}$ (%)	P _{mini} (GPa)
Ca_3N_2	Al	10*	5,2
		100	5,7
Ca_3N_2	B	5*	5,3
		30	5,5
Ca_3N_2	Ti	15*	5,0
		35	5,3
Ca_3N_2	Si	10*	5,5
		30	5,9
Mg_3N_2	Al	25*	5,4
Mg_3N_2	B	10*	5,0
		25	5,2
Li_3N	Al	35*	5,2
		100	5,9
Li_3N	B	10*	5,2
		30	5,9
$30\text{Ca}_3\text{N}_2, 70\text{Li}_3\text{N} \#$	$\begin{matrix} \text{Al} \\ + \\ \text{B} \end{matrix}$	$\begin{matrix} 7 \\ 12 \end{matrix}$	5,0
$75\text{Ca}_3\text{N}_2, 25\text{Li}_3\text{N} \#$	Al	35	5,7

* Minimum %.

Proportions by mass.

The following additives were used:

Product	Purity (%)	Granulometry (μ)	Source
Boron	98	50	Prolabo
Aluminum	99.5	50	Goodfellow
Titanium	99.9	60	Johnson Matthey
Silicon	99.95	40	Johnson Matthey

The catalytic nitrides (Li_3N , Ca_3N_2 , Mg_3N_2 sold by Johnson Matthey) were reground prior to use and sifted to obtain particle dimensions less than 40 μm .

Claims

1. Process for the preparation of single crystals of cubic boron nitride by conversion of hexagonal boron nitride in the presence of a catalyst containing at least one alkaline or alkaline-earth nitride in an HP-HT apparatus by operating under appropriate pressure and temperature conditions, characterized in that at least one additive element chosen from aluminum, boron, silicon, zirconium and titanium is added to said catalyst.
2. Process according to Claim 1, characterized in that one introduces the hexagonal boron nitride in the form of a powder having particle dimensions less than 50 μm and in particular less than 40 μm .
3. Process according to either of the preceding claims, characterized in that one uses a nitride catalyst and an additive element in a powder form having particle dimensions less than 100 μm , and in particular less than 60 μm .
4. Process according to any one of the preceding claims, characterized in that said additive element is mixed with said alkaline or alkaline earth boron nitride prior to introduction into said device.
5. Process according to any one of the preceding claims, characterized in that the ratio by weight of hexagonal boron nitride to the catalyst, including the additive, is in the range from 1 to 20.
6. Process according to any one of the preceding claims, characterized in that the ratio by weight of the additive element to the alkaline or alkaline-earth nitride is in the range of 0.05 to 1.
7. Process according to any one of the preceding claims, characterized in that one operates at a predetermined temperature greater than 1,350°C and less than 2,000°C.
8. Process according to any one of the preceding claims, characterized in that one operates at a predetermined pressure selected between 4.5 and 7 GPa.
9. Process according to any one of the preceding claims, characterized in that one maintains the reactive mixture in selected temperature and pressure conditions for a sufficient, predetermined period of time to allow optimal growth of crystals.
10. Process according to the preceding claim, characterized in that said sufficient period of time is between 1 and 20 minutes, in particular between 1 and 5 minutes.

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FIGURE 1

